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APPLICATION NUMBER: 60/419,390

FILING DATE: *October 17, 2002*

RELATED PCT APPLICATION NUMBER: *PCT/US03/33006*



By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

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EXHIBIT

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10-21-02

60419390.101A/PROV

Approved for use through 10/31/2002. OMB 0851-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE


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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

ev 102704478 us

INVENTOR(S)				
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)		
Daniel Jeffrey J.	Alvarez, Jr. Spiegelman	San Diego, CA San Diego, CA		
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto				
TITLE OF THE INVENTION (500 characters max)				
CO2 PURIFICATION FOR THE SEMICONDUCTOR INDUSTRY				
Direct all correspondence to: CORRESPONDENCE ADDRESS				
<input checked="" type="checkbox"/> Customer Number		<div style="border: 1px solid black; padding: 2px;">27111</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">  </div>		
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<input type="checkbox"/> Firm or Individual Name		PATENT TRADEMARK OFFICE		
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ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification Number of Pages		<input type="checkbox"/> CD(s), Number		
<input checked="" type="checkbox"/> Drawing(s) Number of Sheets		<input checked="" type="checkbox"/> Other (specify)		
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		<div style="border: 1px solid black; padding: 2px;">return postcard</div>		
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT				
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.		FILING FEE AMOUNT (\$)		
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees				
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:		<div style="border: 1px solid black; padding: 2px;">02-4070</div>		
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.		<div style="border: 1px solid black; padding: 2px;">\$80.00</div>		
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
<input type="checkbox"/> No.				
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____				

Respectfully submitted,

SIGNATURE



TYPED or PRINTED NAME

COLLEEN J. McKIERNAN

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619-238-0999

Date

10/17/2002

REGISTRATION NO.

(if appropriate)

Docket Number:

48,570

7184-PA18PR

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

PTO/SB/17 (11-01)

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**FEE TRANSMITTAL
for FY 2002**

Patent fees are subject to annual revision.

☒ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$)

80

Complete if Known

Application Number	unknown
Filing Date	unknown
First Named Inventor	Daniel Alvarez, Jr.
Examiner Name	unknown
Group Art Unit	unknown
Attorney Docket No.	7184-PA18PR

METHOD OF PAYMENT (check all that apply)☒ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None☒ Deposit Account:

Deposit Account Number 02-4070

Deposit Account Name Brown Martin Haller & McClain LL

The Commissioner is authorized to: (check all that apply)

☒ Charge fee(s) indicated below ☒ Credit any overpayments
☒ Charge any additional fee(s) during the pendency of this application
☒ Charge fee(s) indicated below, except for the filing fee to the above identified deposit account.
FEE CALCULATION**1. BASIC FILING FEE**

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
101 740	201 370	Utility filing fee	
106 330	206 165	Design filing fee	
107 510	207 255	Plant filing fee	
108 740	208 370	Reissue filing fee	
114 160	214 80	Provisional filing fee	80

SUBTOTAL (1) (\$)

80

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

Total Claims	Extra Claims	Fee from below	Fee Paid
Independent Claims	-20** =	X	0
Multiple Dependent Claims	-3** =	X	0

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description
103 18	203 9	Claims in excess of 20
102 84	202 42	Independent claims in excess of 3
104 280	204 140	Multiple dependent claim, if not paid
109 84	209 42	** Reissue independent claims over original patent
110 18	210 9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) (\$)

0

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)**3. ADDITIONAL FEES**

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
105 130	205 65	Surcharge - late filing fee or oath	
127 50	227 25	Surcharge - late provisional filing fee or cover sheet	
139 130	139 130	Non-English specification	
147 2,520	147 2,520	For filing a request for <i>ex parte</i> reexamination	
112 920*	112 920*	Requesting publication of SIR prior to Examiner action	
113 1,840*	113 1,840*	Requesting publication of SIR after Examiner action	
115 110	215 55	Extension for reply within first month	
116 400	216 200	Extension for reply within second month	
117 920	217 460	Extension for reply within third month	
118 1,440	218 720	Extension for reply within fourth month	
128 1,960	228 980	Extension for reply within fifth month	
119 320	219 160	Notice of Appeal	
120 320	220 160	Filing a brief in support of an appeal	
121 280	221 140	Request for oral hearing	
138 1,510	138 1,510	Petition to institute a public use proceeding	
140 110	240 55	Petition to revive - unavoidable	
141 1,280	241 640	Petition to revive - unintentional	
142 1,280	242 640	Utility issue fee (or reissue)	
143 460	243 230	Design issue fee	
144 620	244 310	Plant issue fee	
122 130	122 130	Petitions to the Commissioner	
123 50	123 50	Processing fee under 37 CFR 1.17(q)	
126 180	126 180	Submission of Information Disclosure Stmt	
581 40	581 40	Recording each patent assignment per property (times number of properties)	
146 740	246 370	Filing a submission after final rejection (37 CFR § 1.129(a))	
149 740	249 370	For each additional invention to be examined (37 CFR § 1.129(b))	
179 740	279 370	Request for Continued Examination (RCE)	
169 900	169 900	Request for expedited examination of a design application	

Other fee (specify)

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$)

0

SUBMITTED BY

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48,570

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619-238-0999

Signature

Date

10/17/2002

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CO₂ PURIFICATION FOR THE SEMICONDUCTOR INDUSTRY

BACKGROUND OF THE INVENTION

[0001] Carbon dioxide (CO₂) is used in a wide variety of industrial processes and products from the carbonation of beverages to the generation of semiconductors. In the semiconductor industry, CO₂ is used in wafer cleaning, for lens gases, laser gases, particle removal and plasma generation. Various phases of CO₂, liquid, gas and supercritical, are used dependent upon the application. Gases can be readily acquired that are $\geq 99.999\%$ pure (contaminants ≤ 10 parts per million, ppm; Ultra High Purity). There is a need to further purify gases to ≤ 5 parts per billion (ppb) contaminants to meet the current Semiconductor Industry Association guidelines. Future requirements will be for contaminants of ≤ 1 ppb, preferably ≤ 0.1 ppb.

[0002] Precise decontamination protocols depend on the source of the CO₂ gas. However, regardless of the source, some contaminants are more difficult to remove than others including light hydrocarbons ($\leq C_4$), oxygen (O₂) and carbonyl sulfide (COS).

SUMMARY OF THE INVENTION

[0003] The invention is a method for the purification of CO₂ to achieve sufficient purity for use of the CO₂ in the semiconductor industry. The invention comprises the use of a combination of materials to achieve low contaminant levels. Decontamination can take place in any of a number of purification apparatuses including both bed and canister apparatuses. The contaminants of primary concern are O₂, sulfurous contaminants, especially COS, phosphorous containing contaminants, silicon containing contaminants and light hydrocarbons (LHC). Contaminants of secondary concern are nitrogenous contaminants, especially NH₃ and NO_x, and other organic compounds. In the method of the invention, total contaminant levels are reduced to ≤ 5 ppb.

[0004] The invention comprises the use of a combination of two or more metals or a single metal in multiple metallic states to combine properties

of both low and high oxidation state metals. This allows for removal of a broad range of contaminants. Oxidizable contaminants are absorbed on the high oxidation state portion of the material and reducible contaminants are absorbed on the low oxidation state portion of the material. The selection and ratios of metals is dependent upon the source of CO₂ to be decontaminated in conjunction with the contaminants to be removed.

[0005] The method comprises both decontamination of the CO₂ and regeneration of the canisters or beds to both reduce cost and facilitate the method of the invention. Purification comprises contacting the fluid CO₂ with the adsorbent for sufficient time to allow for decontamination. Parameters such as time, flow rate, temperature are determined based on the source gas and the apparatus available. Regeneration serves to return the adsorbents substantially to their original state. Regeneration involves both oxidation, to remove sulfur and other contaminants, and reduction, to prepare materials for oxygen adsorption. Metals are selected that are oxidized and reduced under various conditions to allow for the reduction of one of the adsorbents while retaining the other adsorbent in an oxidized state. Exact methods for regeneration depend on the type of beds, the adsorbents used and the major contaminants in the CO₂.

BRIEF DESCRIPTION OF THE DRAWINGS

- [0006] Figure 1 is an O₂ removal test manifold;
- [0007] Figure 2 is purifier temperature data; and
- [0008] Figure 3 is oxygen removal efficiency data.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

[0009] The invention is a method for the production of highly purified CO₂ containing contaminants at ≤ 5 ppb, preferably ≤ 1 ppb, most preferably ≤ 0.1 ppb, for use in the semiconductor industry. Contaminants of primary concern are O₂, sulfurous contaminants, especially COS, silicon containing contaminants and light hydrocarbons (LHC, ≤ 4 C). Contaminants of secondary concern are nitrogenous compounds, especially NH₃ and NO_x and

other organic compounds.

[0010] The invention comprises the use of a mixture of two or more metals or metallic states as adsorbents. The adsorbents combine properties of both high and low oxidation state metals. This combination can be accomplished by a number of methods. First, two or more metals in different oxidation states can be combined (e.g. Cu/ZnO, Fe/MnO_x). Second, two or more metals in similar oxidation states with sufficiently different properties can be combined (e.g. NiO/TiO_x, PdO/CeO_x). Third, a single metal which has oxidation states that vary throughout the metal can be used (e.g. VO_x). Considerations for selecting the appropriate adsorbent or adsorbents are discussed in the Examples below.

[0011] Regardless of the specific selection of adsorbents, the materials are an intimately co-mingled mixture prepared by impregnation, co-precipitation, sublimation or other relevant techniques. The materials may be supported on or mixed with an inorganic oxide for increased surface area, greater structural integrity, improved flow rate, or to accommodate other physical and mechanical considerations. In a preferred embodiment, the adsorbent has a surface area of at least 50 m²/g, should be able to withstand the high pressure associated with all three fluid phases of CO₂ and should not become entrained in the fluid stream or introduce additional contaminants into the fluid stream. The use of co-mingled adsorbents allows for the removal of a variety of contaminants in a single step rather than having to perform multiple steps of decontamination through different beds or containers.

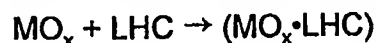
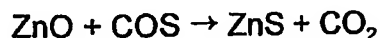
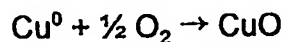
[0012] A variety of purification apparatuses are known including, but not limited to canister and multiple and single bed apparatuses. In a preferred embodiment, the method of the invention is carried out using a dual bed apparatus. Purification comprises contacting the adsorbent material with the CO₂ stream for sufficient time to allow decontamination to the desired level. Decontamination considerations such as time, pressure, flow rate and temperature may be readily determined by those skilled in the art. Decontamination is alternated with regeneration. Frequency and duration of regeneration varies depending on the size of the adsorbent surface area, the

level of contamination of the gas source and a number of other factors well known to those skilled in the art. Regeneration involves oxidation to prepare the material for adsorption of sulfurous and other contaminants and reduction to prepare the material for oxygen adsorption. The exact process of regeneration is dependent upon the adsorbents used and the contaminants that were removed from the CO₂. Such considerations are discussed in the Examples below.

EXAMPLE 1

[0013] *Adsorbents containing two or more metals present in different oxidation states.* Combinations of metals such as Cu/ZnO and Fe/MnO_x are examples. Advantageous materials are those in which the higher oxidation-state portion of the material is reactive towards certain contaminants (e.g. by removing COS in a metathesis reaction that generates CO₂), while the lower oxidation-state portion of the material is reactive towards certain other contaminants (e.g. by absorbing oxygen, hydrogen, or carbon monoxide). Particularly advantageous materials are those in which oxygen readily binds to an oxygen deficient portion of the material (e.g. for kinetic reasons), then diffuses into a co-mingled portion of the material which preferentially binds oxygen (e.g. for thermodynamic reasons). The ratios of the adsorbents to each other can be widely varied depending on the contaminants to be removed as well as other parameters known to those skilled in the art.

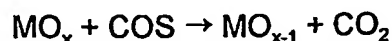
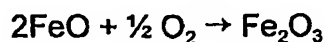
[0014] Cu/ZnO is known to exist as a combination of metallic copper and zinc oxide with Cu present in a substantially reduced state. ZnO is stable fully oxidized Zn^{II} and metal oxides adsorb LHCs. Reactions can proceed as follows during the CO₂ purification method:



Thus, LHCs are removed from the CO₂ stream.

[0015] Similar reactions are possible using Fe/MnO_x, a material which has the properties of a substantially metallic iron mixed with iron and

manganese oxides in widely varying oxidation states. Oxygen-deficient Fe reacts with O₂ and Fe and manganese oxides remove sulfur containing contaminants from the CO₂ stream.

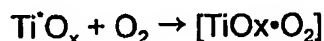
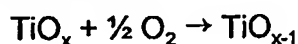


[0016] The combination of Fe/MnO is ideal for the removal of all non-methane hydrocarbons (NMHC) and is particularly suited for the migration of chemisorbed oxygen and sulfur from Fe into bulk Mn.

EXAMPLE 2

[0017] *Adsorbents containing two or more metals present in similar oxidation states, but in which the two metals vary considerably in chemical properties.* Combinations of metals such as NiO/TiO_x and PdO/CeO_x are examples. The aforementioned adsorption properties are still relevant to this material, wherein two portions of the material have different, complementary adsorption properties (e.g. different electronegativities). Rather than the different adsorption tasks being accomplished by similar metals with an oxidation state differential, different portions of the material are in relatively the same oxidation states. The different adsorption properties come from the presence of vastly different metals. An example is a mixture of a late transition metal oxide with an early transition metal oxide. As in the previous case, especially advantageous materials are those that undergo a degree of self-regeneration by diffusion of contaminants adsorbed in one portion of the material into another portion of the material. The ratios of the adsorbents to each other can be widely varied depending on the contaminants to be removed as well as other parameters known to those skilled in the art.

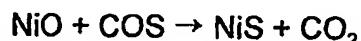
[0018] TiO_x may have oxygen vacancies or be able to adsorb oxygen on exposed metallic active sites. Reactions can proceed as follows during the CO₂ purification method:



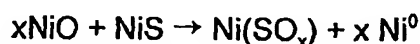
This form may involve bridging dioxygen acting as a ligand rather than

undergoing a redox reaction on a partially reduced titania surface.

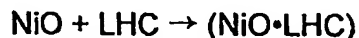
[0019] NiO also may be substantially or partially reduced to Ni⁰, in which case redox chemistry may take place involving the Ni-containing portions of the material. Additionally, the NiO may participate in sulfur scavenging as shown in the following reactions:



[0020] Nickel sulfides/oxides are also known to undergo further disproportionation reactions such as the reaction shown below:



which may generate additional reduced nickel active sites. The ability of NiO to adsorb LHC had not been demonstrated prior to the instant invention. (See Example 5)



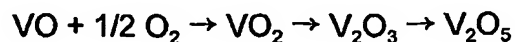
[0021] The various oxidation states of the oxygen-deficient oxides of CeO_x are well-known. Their reactivity is relatively unexplored, but is likely similar to TiO_x and TiO₂ as shown above. Pd and PdO are well known on ceria and display reactivity towards various contaminants in a manner similar to Ni which is in the same periodic group. The combinations of materials in this example function similarly to those of the previous example by providing different reactivities resulting in different adsorption and regeneration properties.

EXAMPLE 3

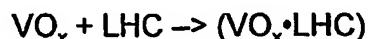
[0022] *Adsorbents containing a single metal oxide in which the metal oxidation state varies throughout the metal.* VO_x is an example of such a metal. The aforementioned adsorption properties are still relevant to this material, wherein two portions of the material have different, complimentary adsorption properties (i.e. different oxidation states). The same metal present in different oxidation states within the material accomplishes the different adsorption tasks. For example, a low oxidation state portion of the material may adsorb oxygen, while a higher oxidation state portion may preferentially

adsorb LHCs or sulfurous contaminants.

[0023] Vanadia based materials in which vanadium is present in several incremental oxidation states are known. For example:



Vanadium sulfides, analogous to the vanadium oxides are also possible. The electropositive surface of vanadia is similar to titania, but with different oxidation characteristics, allowing the reaction:



for the adsorption of LHCs.

[0024] The level of oxidation of vanadium can be controlled during the regeneration process of the invention.

EXAMPLE 4

[0025] *Regeneration of adsorbents.* Regeneration of the adsorbents decreases cost and facilitates the use of the method of the invention. As combinations of metals and metallic states are selected to have various decontamination properties, they are also selected to have different regeneration properties to allow for all of the contaminants to be purged from the adsorbent using heat or cooling in combination with oxygen, followed by reduction under specific conditions to allow only a portion of the adsorbent to undergo reduction.

[0026] An example of this type of reaction would be to first contact the material with an oxidant regeneration gas (e.g. O_2) for a sufficient time and a sufficient temperature to effect removal of all oxidizable contaminants, followed by a second contact with a reductant regeneration gas (e.g. H_2) for sufficient time and at sufficient temperature to produce the desired composition of the material.

[0027] A second example of regeneration encompasses both of the above regeneration steps into a single step. A mixture containing an amount of H_2 , an amount of H_2O and the balance inert gas is contacted with the adsorbent for a sufficient time at a sufficient temperature to return the adsorbent to essentially its original state. This one step regeneration process

saves both time and money.

EXAMPLE 5

[0028] *Oxygen removal efficiency of nickel media exposed to gaseous carbon dioxide.* An analysis was performed to demonstrate that Ni media can remove O₂ from gaseous CO₂. The test purifier consisted of a 70KF body filled with Ni media. The purifier was activated under the same conditions as the inert purifier. Afterwards, the purifier was purged with pre-purified CO₂. The temperature was monitored to indicate when the Ni was done reacting with the CO₂.

[0029] Figure 1 represents the experimental setup. Porter mass flow controllers (MFCs) controlled the flow rates of the 944ppm O₂ standard (Air Products) and the pre-purified house N₂ to attain the desired concentrations. A backpressure regulator (AP Tech) was used to vent during purging of the test manifold. A Nanotrace Oxygen Analyzer (Delta-F) was used to measure the O₂ concentration. The second pre-purified house nitrogen line was used to purge the instrument. A rotameter (Porter) controlled the pressure during the experiment.

[0030] The purifier was tested under the following conditions:

- Challenge Concentration = 1 parts per million (ppm) of O₂
- Flow rate = 3 standard liters per minute (slm)
- Pressure = 30 psig
- Temperature = Ambient

Initially, the challenge gas is allowed to flow through the bypass to the instrument. After 10 minutes the purifier is placed online.

[0031] Figure 2 shows the data gathered when the reduced Ni was exposed to CO₂. The supposition was that the Ni media was fully conditioned with CO₂ when the purifier returned to room temperature.

[0032] Figure 3 shows the data gathered from the Nanotrace. The purifier removed O₂ below 10 parts per billion (ppb) in less than 90 minutes. From extrapolating the data, an O₂ concentration of 5ppb was reached within



3 hours. The purifier has maintained an O₂ concentration below 5ppb for 66.3hours.

[0033] Although an exemplary embodiment of the invention has been described above by way of example only, it will be understood by those skilled in the field that modifications may be made to the disclosed embodiment without departing from the scope of the invention.

ABSTRACT

The invention is a method for the decontamination of CO₂ to a sufficient level of purity to allow it to be used in the semiconductor industry. The invention comprises the exposure of fluid CO₂ to a combination of metals or metallic states under the appropriate conditions for removal of contaminants. The adsorbents are then decontaminated and reduced to allow further rounds of decontamination. The adsorbents are selected to be complimentary to each other, preferentially adsorbing different contaminants. Additionally, the adsorbents are selected to undergo reduction differently such that upon regeneration only a portion of the metals are reduced and the adsorbent is returned essentially to its original state.

Figure 1

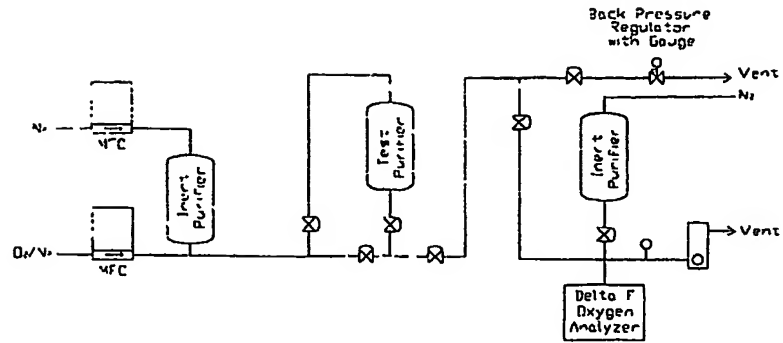


Figure 2

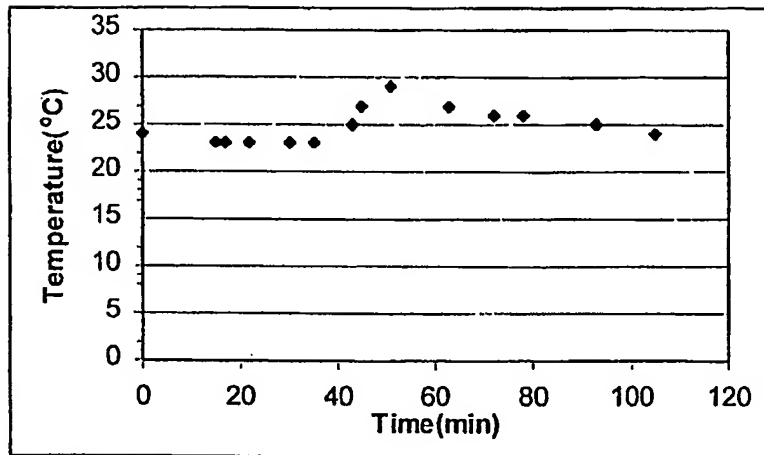


Figure 3

